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Thesis

THE PREPARATION AND IDENTIFICATION OF META-TOLUENE SULFONIC ACID AND OF INTERMEDIATES USED IN ITS PREPARATION.

Submitted by

William Dresbach Hedges

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The Preparation and Identification of meta-Toluene Sulfonic Acid and of Intermediates Used in Its Preparation.

Introduction

Ortho and para- toluene sulfonic acids have been prepared and identified, but the meta toluene sulfonic acid has never been definitely isolated or its properties determined. Hubner and Post [1] mention the solubilities of the barium, lead, calcium, potassium, and sodium salts of the acid and describe their respective crystalline shape. However they fail to mention a means for the conclusive proof of the structures of the compounds obtained. It is my object to prepare the acid as efficiently as possible through simple organic reactions and to make derivatives which will serve as a means of its identification.

In considering the possible methods of preparation it seemed by far simpler to introduce the sulfonic group into the methyl substituted ring than to replace a hydrogen of the acid substituted

1. Journal Chemical Society, 63 , 60 (1874)

ring by a methyl group. The difficulty occurs, of course, in controlling the sulfonation so as to introduce the acid group in the meta position. This reaction has been made to occur by sulfonating para-toluidine and obtaining as one of the products 3-sulfo-4-amino toluene. If the amine group could be removed from this compound and be replaced by a hydrogen, the desired compound would be obtained. It seemed quite probable from a study of the literature with regard to the preparation of the ortho-sulfonic acid that this removal could easily be effected through the diazo reactions. The above brief procedure seemed to offer the most economical and best adaptable method for the preparation of the meta-toluene sulfonic. acid.

Preparation of 3-Sulfo-4-Amino Toluene

Cazeneuve and Moreau[1] suggest a possible means for the preparation of the 3-sulfo-4-amino toluene by heating p,p' ditolyl urea with sulfuric acid at 150° C. However both the ortho and meta acids were produced so it offered no particular advantage over the direct sulfonation of

1. Bulletin de la Societe Chemie "3", 19 , 22 (1893)

the para toluidine as used by Pechmann[1], Metcalf[2], and later by Allen[3]. The raw materials used in the later process are quite cheap and readily avaible.

Two hundred grams of fuming sulfuric acid was placed in a three neck round bottom flask equipped with a mechanical stirrer and thermometer. To this acid was added 100 gr. of finely powdered para-toluidine over a period of ten minutes. Agreeing with Allen, the maximum temperature (185°C.) was reached when about one half of the toluidine had been added. Upon the addition of all of the toluidine the mixture was stirred and maintained at the maximum temperature for one hour. The mixture was then poured into an evaporating dish containing an equal volume of cold water and allowed to stand over night. The evaporating dish, the next day, was filled with a mass of light brown crystals. These were filtered by suction and the filtrate permitted to stand for three weeks. At the end of this time there were a few small,flat, needle-like crystals in the

1. Journal Chemical Society, 64, 78 (1875)
2. American Chemical Journal, 15, 301 (1893)
3. M. A. Thesis, 1920 - Boston University

solution. These di-sulfonic acid crystals were obtained by Metcalf (loc. cit.) after the filtrate had stood for an equal length of time. Allen reported that after his solution had stood for four weeks these crystals failed to appear.

The residue, resulting from the suction filtration and containing the ortho and meta-sulfonic acids, was dissolved in 10 liters of water. This dilute solution was then neutralized with barium hydroxide. After the neutralization was complete the solution was evaporated to a volume of approximately 200 cc. by which time a thin brown crust had appeared on top of the liquid. The solution upon cooling became filled with a mass of light brown granular particles. The solution was filtered and the residue studied under the microscope in an effort to determine whether two kinds of crystals were present. No distinct crystals could be distinguished and the general appearance was the same. These crystals were dissolved in water and dilute sulfuric added until a precipitate of barium sulfate was no longer obtained. The barium sulfate was removed

by suction filtration using a heavy asbestos pad as the filtering medium. A clear light yellow solution was obtained. From this solution upon evaporation was obtained a mass of light yellow crystals. These crystals, supposedly a mixture of the free sulfonic acids, were examined under the microscope and two distinct types were noted, (Fig. 1.). One type appeared as thin square plates while interspersed among these were a few small needle like crystals. Metcalf (loc. cit.) and

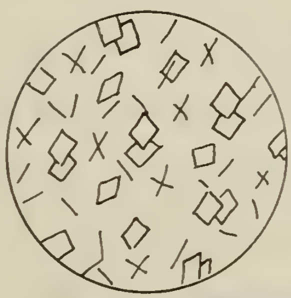

Fig. 1.

other investigators claimed that the 3-sulfo-4-amino toluene crystallized in small needles and that 2-sulfo 4-amino-toluene crystallized as plates, while Allen was unable to detect any needle like crystals.

The yield of the small needles seemed to be very poor.

In an effort to reach a better yield of the supposedly 3-sulfo-4-amino toluene the above procedure was repeated with a few modifications. Pechmann (loc. cit.) claims that during the sulfonation process more of the 2-sulfo-4-amino toluene is formed if the mixture is heated for a considerable length of time. It seemed quite probable that the yield of the meta could be increased if the acid solution was not heated for so long a period. Accordingly 200 gr. of the para-toluidine was added to 400 gr. of the concentrated sulfuric acid, all of the toluidine being added in about fifteen minutes. The maximum temperature reached was 210°C. The mixture was allowed to cool to about 180°C. and the temperature maintained at that point for fifteen minutes. The solution was allowed to crystallize as before and the resulting crystals were dissolved in 20 liters of water. A saturated solution of barium hydroxide was added until a clear sample of the dilute

acid solution no longer gave a precipitate of barium sulfate, approximately 420 gr. being required. Dilute sulfuric acid was then added until all of the excess barium had been precipitated as shown by a small amount of the solution tested in a test tube. The barium salts of the sulfonic acids are soluble in water solution of the above concentration so that the above outside tests used in freeing the solution of sulfuric acid are quite efficient. The barium sulfate was removed by suction filtration as before, and the solution evaporated to a volume of approximately 300 cc. Upon examining a drop of the above concentrated solution under a microscope two types of crystals were easily distinguishable. The first crop of crystals was light yellow and was separated from the mother liquor by suction, and the filtrate evaporated to a volume of about 150 cc. During this evaporation the color of the solution changed from a medium yellow to a dark brown. The mixture of the crystals obtained from this solution resembled the first crop in size and shape, but were darker in color and

and there seemed to be fewer needles in proportion to the flat crystals. The remaining mother liquor was further evaporated to a volume of about 50 cc. The crystals obtained from this evaporation had the same dark brown color as those of the previous crop, but upon examining them under the microscope there seemed to be only the flat crystals present.

Some of the crystals obtained in the first sulfonation process had been examined in an effort to determine whether they were colored in the pure state or whether the color was due to impurities. The mixture of light yellow crystals was placed in aqueous solution and boiled with activated charcoal (Norite) for about a half hour. Upon filtering and allowing to cool, crystals of the same light yellow color were obtained. These crystals were again subjected to the same treatment but no futher decoloration was noted. The second and third crops of crystals obtained from the second sulfonation were likewise treated with the activated charcoal and the light yellow crystals obtained.

From 200 gr. of para-toluidine about 150 gr. of the purified mixture of the two sulfonin acids was obtained.

In subsequent preparations of the sulfonic acids the conditions were varied in an attempt to increase the yield of the 3-sulfo-4-amino toluene. However, when the temperature was much less than 180°C and held constant for less than half an hour it was found that the sulfonation of the toluidine was incomplete. It seemed then that the temperature and time of heating used in the second sulfonation give the most desirable results.

Separation of the 3-Sulfo-4-Amino-Toluene and 2-Sulfo-4-Amino-Toluene

Allen(loc. cit.) claimed that the two types of crystals obtained by him were quite effectively separated by screening them. However the mixture that he obtained consisted of hard square brown crystals and a light powdery mass. This method seemed quite impractical as a means of separating the crystals I obtained so other means were sought. Metcalf (loc. cit.)

suggests that the crystals may be separated by means of their specific gravities in a 50% alcoholic solution. Although the separation of the two forms by means of differences in their specific gravities is highly improbable - it was found to be impossible- it did seem advisable to attempt to separate them by means of their possibly different solubilities in alcohol. A few crystals were placed in absolute alcohol, and upon examining the liquid it seemed that only the finer needle like crystals had dissolved. The solution was filtered and a portion of the filtrate was allowed to crystallize upon the microscope slide. The crystals thus obtained were found to consist only of the needle like forms and from the describtions given by previous investigators were thought to be the 3-sulfo-4-amino-toluene(Fig. 2). Upon examining the insoluble portion only the square flat forms were noted. (Fig. 3). From further search of the literature, it was found that Metcalf (loc. cit.)

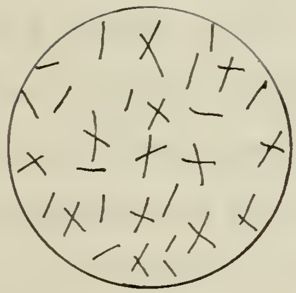

Fig 2

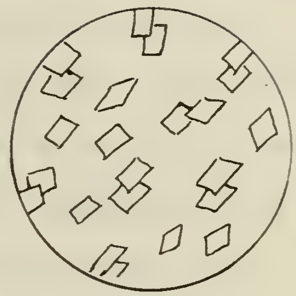

Fig 3

had also suggested the separation of the crystals by means of different solubilities in dilute alcohol solution. As the needle like crystals were only sparingly soluble in the absolute alcohol, 95% alcohol was tried. In this solution the solubility of the needles was greatly increased and upon studying the recrystallized product under the microscope none of the flat crystals were noted.

The above method seemed quite satisfactory as a mea ns of separating the two isomers. The 150 gr. of the purified crystals was refluxed with 2 liters of 95% alcohol.

The undissolved portion was separated, and by distillation from a water bath the volume of the alcoholic solution was reduced to about 500 cc. Upon cooling, a heavy precipitate of needle like crystals was obtained. Examination of them under the microscope showed no trace of the flat crystals. The crystals thus obtained were washed with ether and dried. The yield was about 19 gr. of the desired product. The mother liquor was further evaporated to a volume of about 200 cc. The appearance of the solution had become much darker and the resulting crystals were of a medium brown color as compared to the light yellow crystals obtained at first. However, in spite of the color, the shape of the crystals appeared the same. A water solution of these crystals was boiled with some of the Norit previously used, and crystals were obtained which were only slightly darker than those crystallized

from the alcoholic solution. The two crops of crystals, one crystallized from an alcoholic solution and the other from the aqueous solution seemed to be from general observations the same compound. The weight of the combined crops was 54 gr. resulting in a yield of 14.4% based on the amount of para toluidine used. Allen (loc. cit.) said that his yield under conditions which corresponded to those of my first preparation was about 10%.

Identification of 3-Sulfo-4-Amino Toluene

The sulfonic acid obtained in the preceding preparation had no melting point, but upon heating the acid to about 290°C. it turned brown. Pechmann(loc. cit.) states that the 3-sulfo-4-amino toluene decomposes at 130°C , Later investigators, namely,

John R. Scott and Julius B. Cohen[1] state that the acid turns brown at 290° C and that it becomes a blackish mass 312° C. In their article they also give the decomposition temperatures of both the ammonium and aniline salts.

An attempt was made to prepare a derivative of the acid which would give a definite melting point. However up to the present it has been unsuccessful. The first derivative attempted was the acetyl derivative. Two cc. of acetyl chloride was placed in a test tube and about .5 gr of the finely powdered acid was added. No apparent reaction resulted and the mixture was allowed to stand over night. The acid had settled to the bottom of the test tube but no further change was noted. A similar mixture was refluxed for two hours, but again no apparent change was noted in acid. An effort to make the benzoyl

1. Journal Chemical Society T. 121 789 (1922)

derivative was next attempted but it likewise proved fruitless. The benzoyl chloride together with dilute sodium hydroxide was placed in the test tube and the acid added. Upon shaking the mixture a small amount of heat was evolved. In about fifteen minutes a heavy precipitate separated out,which looked very much like benzoic acid. The solution was filtered and the precipitate dried. A melting point proved it to be only benzoic acid as was at first suspected. Thinking that the derivative might be soluble in the above solution, HCl was bubbled through it for several minutes. However no precipitate resulted. In a further attempt to make an acetyl derivative the acid was dissolved in acetic anhydride. The solution was then refluxed for 2 hours and upon cooling a precipitate appeared. This precipitate was twice recrystallized from water and its

melting point taken. Decomposition occurred, however, at 236° C. Scott and Cohen (loc. cit.) prepared a condensation product of the 3-sulfo-4-amino toluene with isocyanic acid. The para carbamido-toluene meta sulfonic acid thus obtained became yellow at 210°C and decomposed at 222°-223°C. At the time of publication of their article they had no definite proof of the exact formula. Allen (loc, cit.) converted the acid through the diazo reaction to the cresol sulfonic acid and thus obtained a compound witha definite melting point.

Several color tests have been advanced as a means of distinguishing between the 3-sulfo 4-amino and 2-sulfo-4-amino toluenes. J. V. Janovsky [1] claimed that upon treating an aqueous solution of the 2-sulfo-4-amino toluene with lead peroxide a yellowish red solution resulted, and upon treating a similar solution of the 3-sulfo-4-amino toluene with the same reagent a wine red solution resulted. These color tests were

1. Journal Chemical Society,A. 76,936 (1888)

made and found to agree with his obser-
vations. However great care must be taken so as to obtain solutions of the same concentrations, as the shade is sometimes obliviated by the intensity of the color. Pechmann (loc. cit.) states that the 2-sulfo-4-amino toluene when treated in a similar manner will give a bluish red color. These color tests were also tried and the results agreed with those described in the literature. E. A. Schnieder[1] suggests that the two isomers can be distinguished by the solubilities of the potassium salt in aqueous solution. He claims that the potassium salt of the 3-sulfo-4-amino-toluene is insoluble in a cold caustic potash solution while the potassium salt of the 2-sulfo-4-amino-toluene is soluble at all temperatures. As yet these tests have not been confirmed.

Tests for nitrogen and sulfur were made in the usual way and positive results obtained in each case. The solubility of the 3-sulfo-4-amino-toluene in some of the more common solvents was determined with the following results.

1. American Chemical Journal 8, 274 (1886)

It was found to be very soluble in hot water, slightly soluble in cold, slightly soluble in cold absolute alcohol, soluble in hot absolute alcohol, soluble in chloroform and acetone, but insoluble in ether, ligroin, petroleum ether, and carbon tetrachloride.

It was suggested (page 9) that the two acids originally obtained might be separated by their difference in specific gravities. An attempt was therefore made to determine the specific gravity of each acid by placing them in unreactive liquids until one was obtained in which the acid remained suspended. By determining the specific gravity of the liquid one would have that of the acid. Both of the acids proved to have a greater specific gravity than ligroin and to be lighter than carbon tetrachloride. Therefore these two substances were mixed in various proportions in an effort to find a solution in which the 3-sulfo-4-amino toluene would remain

suspended. This mixture was found to consist of 10 cc. of carbon tetrachloride and 0.8 cc. of ligroin, having a specific gravity of approximately 1.519. Some of the 2-sulfo-4-amino toluene was added to this mixture and it seemed to remain in suspension as well as 3-sulfo-4-amino-toluene. After standing several days, however, the 2-sulfo-4-amino toluene had for the greater part settled to the bottom portion of the mixture indicating that it possesed a slightly greater specific gravity. A solution containing 10 cc. of carbon tetrachloride and 0.7 cc. of ligroin and having a specific gravity of about 1.523 seemed more nearly to have the same specific gravity as the 2-sulfo-4-amino toluene. As the method used for determining the specific gravity of the liquid is hardly accurate to the fourth significant figure, the values given are more or less approximate ones. However, I think it is evident that the separation of the two acids by means of their specific

gravities would indeed be a difficult task.

It was suggested that the index of refraction might furnish an identifying constant for the 3-sulfo-4-amino toluene. The index of refraction was determined microscopically by immersion methods making use of the Becke line. When a crystal is immersed in a liquid and the mixture viewed through a microscope dark or colored halos appear at the boundaries of the two phases providing the two substances do not have the same indices of refraction . The Becke line is the bright band of light outlining a crystal of vertical planes immersed in a liquid when the whole is illuminated. If the focus of the microscope is raised the bright halo will move toward the medium of higher index of refraction. The 3-sulfo-4-amino toluene was first immersed in nitrobenzene and the acid was found to have the higher index of refraction. Upon immersing the acid in cassia oil it was found that the cassia oil had the higher refractive index.

Mixtures of various proportions of these two liquids were then treated until a mixture was obtained which seemed to have the same index of refraction as the acid. The refractive index of this mixture was then determined by the refractometer and found to be 1.597. In a similar manner an attempt was made to determine the refractive index of the 2-sulfo-4-amino toluene. It was found to be between 1.628 and 1.658, but due to lack of liquid with the higher refractive index a more accurate determination could not be made.

As a further means of establishing the identity of the 3-sulfo-4-amino toluene a quantitative analysis was made for nitrogen and sulfur. Nitrogen was determined by the usual Kjeldahl procedure and the sulfur was oxidized to the sulfate in a Burgess-Parr sulfur bomb and then precipitated and weighed as the barium salt. The following results were obtained:

	Experimental		Theorectical
	I	II	
Sulfur	17.16%	18.13%	17.11%
Nitrogen	7.50%	7.11%	7.48%

Diazotization and Reduction of the Diazonium Chloride of 3-Sulfo-4-Amino-Toluene

As far as could be ascertained all previous experimentors in an effort to obtain the meta - - toluene sulfonic acid had boiled the diazonium salt in an alcoholic solution. Some of the early investigators in using ethyl alcohol for this purpose had obtained a brown pasty substance which they thought to be the 3-sulfo-4-amino-toluene. Metcalf(loc. cit.) in following the same procedure obtained the pasty like mass and identified it as the ethoxy-sulfo-toluene. Allen (loc. cit.) prepared the diazonium salt of the 2-sulfo-4-amino-toluene and claimed to have successfully replaced the diazonium group by hydrogen upon boiling with normal butyl alcohol in the presence of

sodium carbonate. He obtained a yellowish orange porous solid but was unable to identify it. R. Bracket and C. Hayes [1] prepared the ortho toluene sulfonic acid by converting the diazonium salt into the hydrazine and then removing the hydrazine group. From descriptions of their work they seemed to have obtained a fair yield. I therefor attempted to repeat their work using the 3-sulfo-4-amino-toluene.

Two gr. of the 3-sulfo-4-amino-toluene was placed in about 10 cc of water. The acid did not completely dissolve in the cold liquid but the undissolved portion remained in suspension. To this aqueous suspension, surrounded by an ice bath was added 1.2 cc of sulfuric acid (sp. gr. 1.84). Upon the addition of the acid all of the sulfonic acid dissolved and the remaining solution was colored a light orange. To this cold solution was added 1 gr. of potassium nitrite dissolved in a few cc of water. When the solutions were mixed a slight amount of gas was evolved, and the color of the solution changed to a dark orange.

1. American Chemical Journal 9,400,(1887)

The whole reaction was carried out at a temperature under 5°C. Complete diazotization was tested for with potassium iodide paper.

The so called Stecker-Romer method as described by Brackett and Hayes (loc. cit.) was used for the preparation of the hydrazine. A solution consisting of 2.7 parts of sodium carbonate and 5 parts of water was saturated with sulfur dioxide. This solution was just made alkaline by the addition of sodium hydroxide. About 10 cc. of the above solution was added to the cold diazonium solution. This mixture was then heated on a steam bath for approximately 15 minutes and during this time the solution assumed a pinkish tint. Ten cc. more of the sulfite solution was added and then the whole acidified with hydrochloric acid. Upon cooling, small needle like crystals separated out. These were filtered and examined under the microscope and gave one the impression that they were organic crystals. After heating them for a few moments, complete combustion resulted.

Twenty grams of the 3-sulfo-4-amino-toluene was treated in the same manner and similar crystals obtained. The yield however was very small, obtaining

only about 5 grams of product (supposedly the hydrazine) from the 20 gr. of the original acid. Attempts were made to extract more of the compound from the mother liquor but were unsuccessful.

In an attempt to obtain better yields of the hydrazine other methods of reducing the diazonium compound were tried. The one found to be the most satisfactory but still giving a very low yield made use of stannous chloride as the reducing agent. A solution of stannous chloride in cold concentrated hydrochloric acid was added to a cold diazonium solution prepared from 17 gr. of 3-sulfo-4-amino-toluene. The resulting mixture became a light coffee color and the solution seemed filled with light tan crystals. Upon filtering and drying however there was only about 7 gr. of product. The chief advantage of this later procedure did not lie in the increased yield, but in the ease of manipulation. It seemed that there would be considerable of the hydrazine hydrochloride remaining in the brown solution, but great difficulty was encountered in

attempts to extract it. It was impossible to separate the hydrazine by decomposing the hydrochloride through the addition of a base for the soluble sulfonic salt would be formed. It seemed quite possible that the tin might be removed by precipitating it as the sulfide. This was tried and the resulting light yellow solution evaporated to a smaller volume. The addition of ammonium hydroxide did not form a precipitate so it was concluded that the ammonium salt of the 3-sulfo-4-hydrazino-toluene was soluble in an aqueous solution. A very few inorganic salts of 3-sulfo-4-hydrazino-toluene are soluble inthe more common organic solvents so an extraction of the hydrazine could not be obtained from a basic solution in this manner. Likewise in an acid solution the acid salt is formed so an extraction by an organic solvent was not likely to be possible in an acid medium. A successful separation and isolation of the hydrazine from this solution was not made.

From the above preparations of the hydrazine hydrochloride it seemed that it might be better

if as many of the inorganic reagents as possible could be eliminated. It also seemed advisable to oxidize the hydrazine in the original solution in which it was prepared. Such a scheme would greatly increase the efficiency of the preparation and would make the separation of the meta toluene sulfonic acid no more difficult.

Identification of the Hydrochloride of 3-Sulfo-4-Hydrazino Toluene

The literature offered very little help in suggesting simple means for the identification of the compound. A melting point was attempted but it was found that the hydrazine decomposed between 125° and 127° C. Elementary analysis showed the presence of sulfur, nitrogen, and chlorine. The usual sodium fusion test failed to give a positive test for nitrogen, however.

Likewise negative results were obtained when the same precedure was followed in testing for nitrogen in phenylhydrazine. Lassar-Cohn in his book bearing the title "Organic Laboratory Methods" suggests the use of a mixture of magnesium and potassium carbonate for the fusion of the unknown instead of the free metallic sodium. This fusion mixture was tried and a positive test for nitrogen was obtained. The hydrazine was also heated with soda lime and t e evolution of ammonia was detected.

Some of the hydrochloride of 3-sulfo-4-hydrazino toluene obtained from the preceding preparations was thoroughly washed with alcohol and dried. This sample was then analyzed for the sulfur and nitrogen content. The Burgess-Parr sulfur bomb was again used for the determination of sulfur, and nitrogen was determined by a modified Kjeldahl procedure as suggested by Allen [1]. By this method the hydrazine was reduced by sugar, but instead of using micro quanities as Allen advised the usual amounts of material were used. The results

1. American Chemical Society Journal 52 2958 (1930)

of the analysis are given in the following table.

	Experimental		Theoretical
	I	II	
Nitrogen	11.15%	11.16%	11.76%
Sulfur	13.7%	13.9%	13.6%

The theoretical results were computed upon the assumption that the compound analyzed was the hydrochloride of 3-sulfo-4-hydrazino toluene.

Preparation of Meta Toluene Sulfonic Acid

From the small amounts of the hydrazine obtained in the preceding work an attempt was made to prepare the free acid. Two methods were used, (1) the use of copper sulfate as the oxidizing agent and (2) the use of ferric chloride as the oxidizing agent. Brackett and Hayes (loc. cit)

used the method of Haller in converting the hydrazine to the ortho toluene sulfonic acid. The hydrazine was heated with 10% copper sulfate solution. The copper oxide thus formed was filtered from the solution and the filtrate neutralized with chalk. The excess calcium ion was then removed by the addition of sodium carbonate. The solution was then filtered and evaporated to dryness. Upon studying the residue there seemed to remain only inorganic salts.

No better results were obtained when the ferric chloride was used. The theoretical amount of ferric chloride was placed in solution and slightly acidified. To this acid solution was added the hydrazine. As the reaction proceeded the color of the solution changed from a yellowish brown to a greenish shade. The iron was precipitated as the hydroxide by the addition of ammonium hydroxide. The clear filtrate, obtained after the iron had been separated, was evaporated to dryness over a steam bath. The ammonium chloride thus obtained upon standing

in a covered dish became brown. This change in color seemed to indicate the presence of some foreign matter which might have been the desired acid.

As was suggested earlier in this paper it seemed that the preparation might be more efficient if the hydrazine was not separated from the original solution but oxidized directly. Consequently in the following attempts to isolate the acid this scheme was followed. The hydrazine was prepared in the usual way using the stannous chloride as the reducing agent. However the solution was diluted so that none of the hydrazine would precipitate as the hydrochloride. To this solution was then added an excess of ferric chloride and the whole boiled until complete oxidation was assured. The solution was then made alkaline with ammonium hydroxide precipitating both the iron and the tin. Due to the tendency of the ferric hydroxide to exist in the colloidal state great difficulty was encountered in free-

ing the solution from the iron, but after repeated digestions over a small flame most of the iron was removed. The solution was next just acidified with hydrochloric acid. Presumably, the solution at this point contained ammonium chloride, potassium chloride, arising from the potassium nitrite originally used, and the free sulfonic acid. It seemed that the greater part of the ammonium chloride might be removed by boiling the solution with lead carbonate. Such a procedure was attempted and after several hours of vigorous boiling all traces of ammonia had disappeared, and a considerable quantity of lead chloride was filtered from the cold solution. During this process it was possible that the lead salt of the meta toluene sulfonic acid might have been formed. It seemed reasonable to expect that sulfuric acid, if added to the solution, would free the meta toluene sulfonic acid and precipitate the lead as the sulfate. Such was found to be the case for upon the addition of the acid a quantity of white

precipitate was formed. In order to remove the excess sulfuric acid barium hydroxide was added until a precipitate no longer formed. In the solution at this point there should be dissolved the free acid, potassium carbonate and perhaps some potassium chloride with traces of other salts. The above solution was evaporated to a volume of about 100 cc. Upon cooling, a crystalline substance separated out which, when studied under the microscope, seemed to consist chiefly of needle-like crystals.

An attempt was made to extract these crystals by various organic solvents. Among the solvents tried were carbon tetrachloride, acetone, ethyl-acetate, ether, ligroin, benzene, and toluene. The above solvents had no effect either in the hot or cold. Hot ethyl alcohol did however dissolve a portion of this crystalline mass. This soluble portion was recrystallized twice from hot absolute alcohol and a very light yellow substance was obtained.

This material was acidic and gave a neutral equivalent of 340 or just about twice that which

the pure sulfonic acid should have given.
An elementary analysis showed the presence of sulfur, absence of nitrogen, and traces of chlorides. The material did not have a definite melting point but decomposed, turning to a dark mass at about 250°C. Upon burning only a very small amount of ash remained.

The above properties seemed to indicate that if the acid were present at all, it was only with considerable impurities. It was thought that the material could be further purified by converting the acid to the chloride and then to the amide. In attempting to follow this procedure the acidic material was heated with thionyl chloride but no apparent reaction took place. The material was next placed in a round bottom flask equipped with condenser and thoroughly mixed with powdered phosphorous pentachloride. By means of an oil bath the temperature of this mixture was maintained between 170° and 180°C for about five hours.
At the end of this period the mass in the flask had become brown, but there was no other

evidence of a chemical reaction having taken place. The phosphorous pentachloride was decomposed with water and the resulting brown muddy solution extracted with ether. The ether became brown even after five extractions had been made. The ether wasthen distilled and a slight amount of oil remained. This oil had an odor somewhat like that of benzene sulfonyl chloride, but there was not a sufficient quantity of the material to determine other physical constants or to make an analysis for the elements.

During the extraction of the aqueous solution with ether a portion of the ether was permitted to remain in contact with the muddy solution over night. At the junction of the two layers a very viscous material was formed. This substance was not investigated further, but it seemed quite reasonable to suspect that it might contain some meta toluene sulfonyl chloride.

Summary

Up to this time the meta toluene sulfonic acid has not been satisfactorily prepared, but a substance was obtained whose prope ties seemed to indicate that there was some free organic acid present and it is quite probable that this was the desired acid.

In spite of the fact that the acid was not satisfactorily prepared, I believe that progress was made in the method under consideration, and that it is quite possible to prepare the acid in this manner. The chief difficulties occur in separating the acid from the solution in which it was prepared. It is hard to extract it from the aqueous solution because of its apparently great solubility in water and insolubility in the common organic solvents. The other method of isolating the free acid from the mother liquor must necessarily consist of eliminating the inorganic salts present present and evaporating the remaining liquid, or of precipitating the acid as an insoluble salt. Most of the salts of sulfonic acids are soluble in water solution and the elimination of the

other inorganic salts often involves a waste of material and even then is not efficient.

In regard to the intermediates used in this preparation, a practical means for the separation of 2-sulfo-4-amino-toluene and 3-sulfo-4-amino-toluene was established. By analysis the composition of the hydrochloride of 3-sulfo-4-hydrazino-toluene was determined and its identity established.

BIBLIGRAPHY

F. Allen, M. A. Thesis (1920)

Am. Chem. Soc. Jour. 52, 2958 (1930)

H. L. Buff, Ber. 3, 796 (1870)

Brackett and Hayes, Am. Chem. Jour. 9, 400 (1887)

Caseneuve and Moreau, Bull. de la Soc. Chim."3" 19, 22(1898)

Chamot and Mason, Handbook of Chemical Microscopy,
John Wiley & Sons, Inc. 1930

D'Able, Richter's Organic Chemistry, Vol. 11
P. Blackiston & Co. 1922

Fisher, Laboratory Manual of Organic Chemistry,
John Wiley & Sons, 1920

Hopper, Cumming, Wheeler Systematic Organic Chemistry,
D. Van Nostrand Co. 1924

Hubner and Post, Jour. Chem. Soc. 63, 60 (1874)

Janovsky, Jour Chem Soc. A. 76,,936 (1888)

Kamm, Qualitative Organic Analysis
John Wiley & Sons 1922(reprint)

Lassar-Cohn, Organic Laboratory Methods, Tran. Cesper
Williams & Wilkins Co. 1928

Metcalf, Am.Chem.Jour. 15, 301 (1893)

Neville and Winther, Jour. Chem. Soc. T 69, 625 (1880)

Pechmann, Jour. Chem. Soc. 64, 78(1875)

Scott and Cohn, Jour. Chem. Soc. T. 121, 789 (1922)

Spielmann, Richter's Organic Chemistry, Vol. 1
P. Blackistons & Co. 1918

Schnieder, Am. Chem. Jour. 8, 274 (1886)

Organic Synthisis, Roger Adams and others,

John Wiley & Sons